Using Natural ^{210}Pb and its Daughters (^{210}Bi and ^{210}Po) to Estimate Aerosol Residence Times

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References

1. J.S. Gaffney, K.A. Orlandini, N.A. Marley, and C.J. Popp, "Measurement of ^{7}Be and ^{210}Pb in Rain, Snow, and Hail." *J. Appl. Meteorol.* **33** 869-873 (1994), and references therein.
2. J.S. Gaffney, K.A. Orlandini, N.A. Marley, and C.J. Popp, "Reply to Comments on 'Measurement of ^{7}Be and ^{210}Pb in Rain, Snow, and Hail.'" *J. Appl. Meteorol.* **34** 2106-2109 (1995).
3. N.A. Marley, J.S. Gaffney, K.A. Orlandini, P.J. Drayton, and M.M. Cunningham, "An Improved Method for the Separation of ^{210}Bi and ^{210}Po from ^{210}Pb Using Solid Phase Extraction Disk Membranes: Environmental Applications." *Radiochim. Acta* **85** 71-78 (1999).
4. N.A. Marley, J.S. Gaffney, M.M. Cunningham, K.A. Orlandini, R. Paode, and P.J. Drayton, "Measurement of ^{210}Pb, ^{210}Po, and ^{210}Bi in Size Fractionated Atmospheric Aerosols: An Estimate of Fine Aerosol Residence Times." *Aerosol Sci. Technol.* **32** 569-583 (2000), and references therein.
5. M. Baskaran and G.E. Shaw, "Residence Time of Arctic Haze Aerosols using the Concentrations and Activity Ratios of ^{210}Po, ^{210}Pb and ^{7}Be." *J. Aerosol Sci.* **32** 443-452 (2001).

URBAN AIR QUALITY – KEY ISSUES

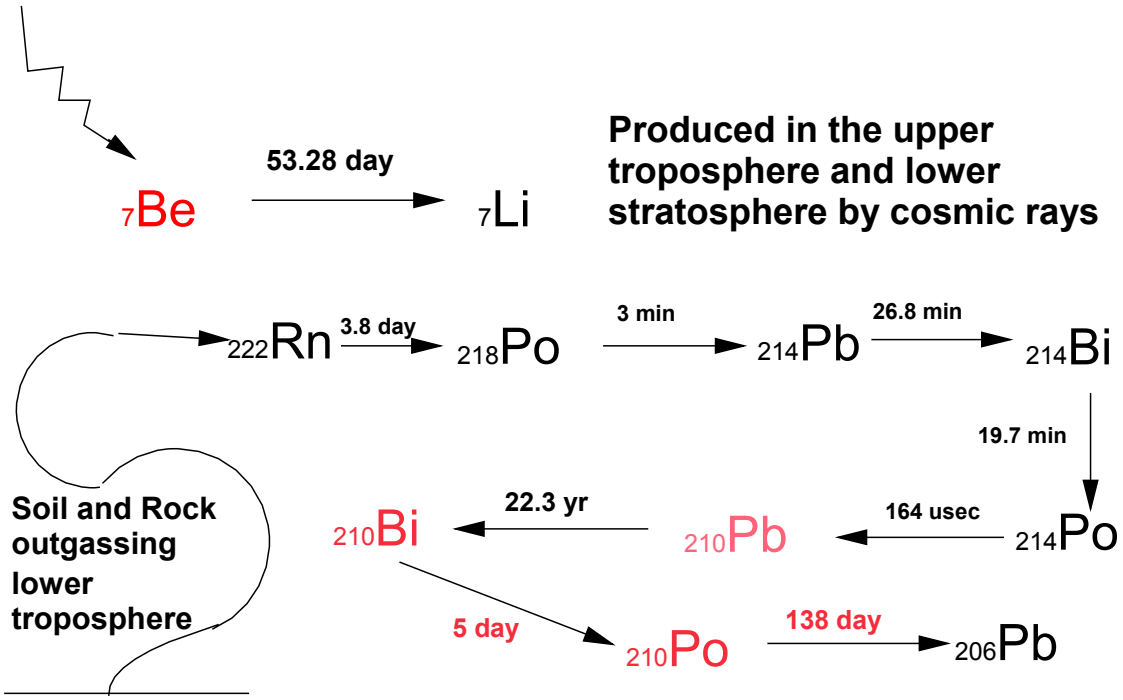
Photochemical Smog – Ozone and Aerosols

Health Impacts – Increases in :

- Premature Deaths
- Asthma
- Chronic Bronchitis
- Decreased Lung Function – Difficulty Breathing
- Respiratory Cases at Hospitals and Emergency Rooms
- Work and School Absences

Climate Impacts – Urban Heat Island Effects !

Radioactive Decay of Natural Atmospheric Tracers



Estimation of Aerosol Residence Times

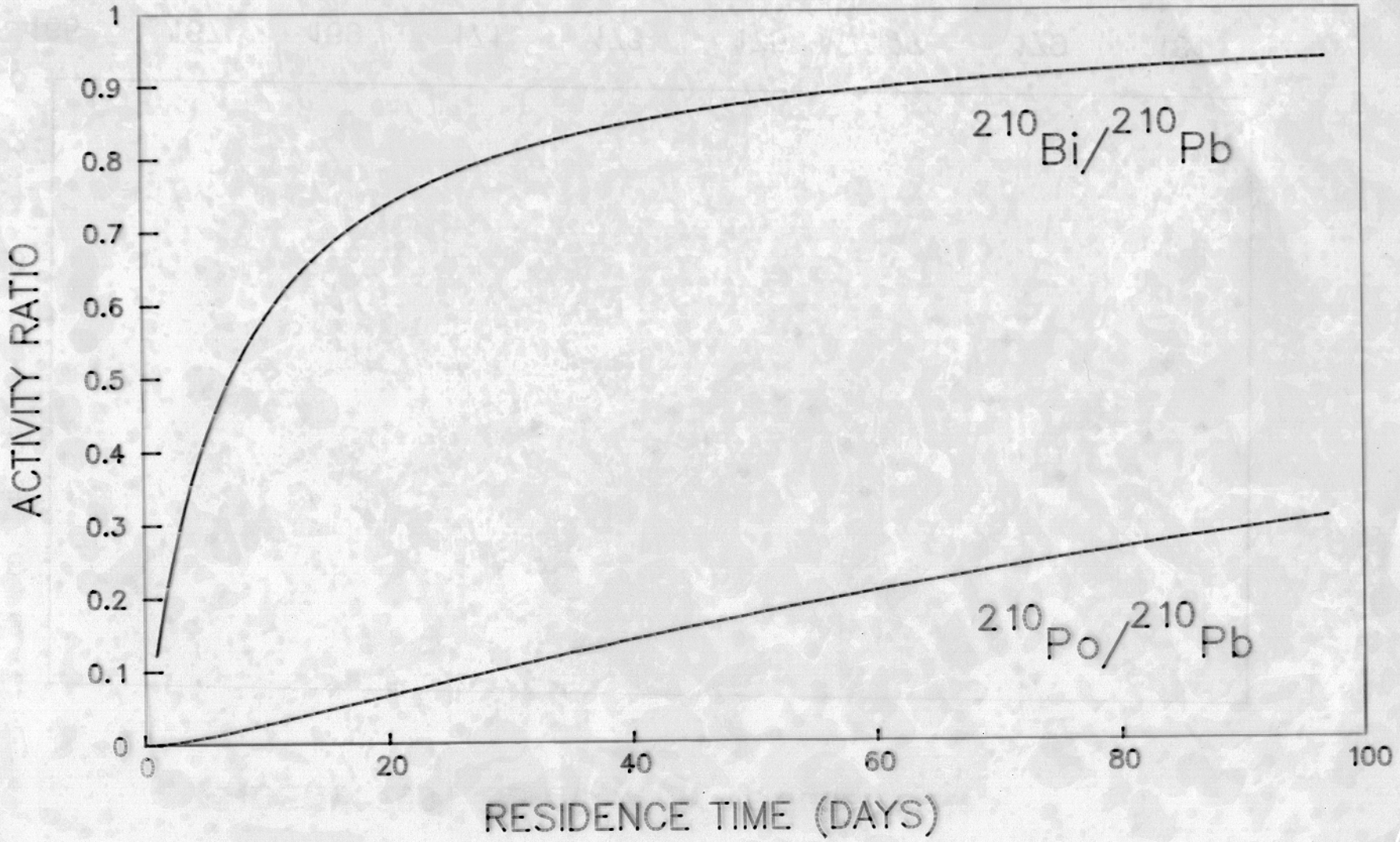
Based upon the radioactive decay times for the ^{210}Pb daughters, the change in mean residence time of an atmospheric aerosol (T_R) can be calculated as the reciprocal of the aerosol removal constant from the atmosphere ($1/\lambda_R$) from the following equation:

$$A^{210}Po/A^{210}Pb = T^2_R/(T_R+7.2)(T_R+200)$$

Where $A^{210}Po$ and $A^{210}Pb$ are the respective activities of the two radioactive elements in the sample.

(See Nevissi, A.E. (1991) J. Radionanal. Nucl. Chem. 148:121-131.)

Activity Ratio vs Residence Time for Aerosols Removed in Precipitation



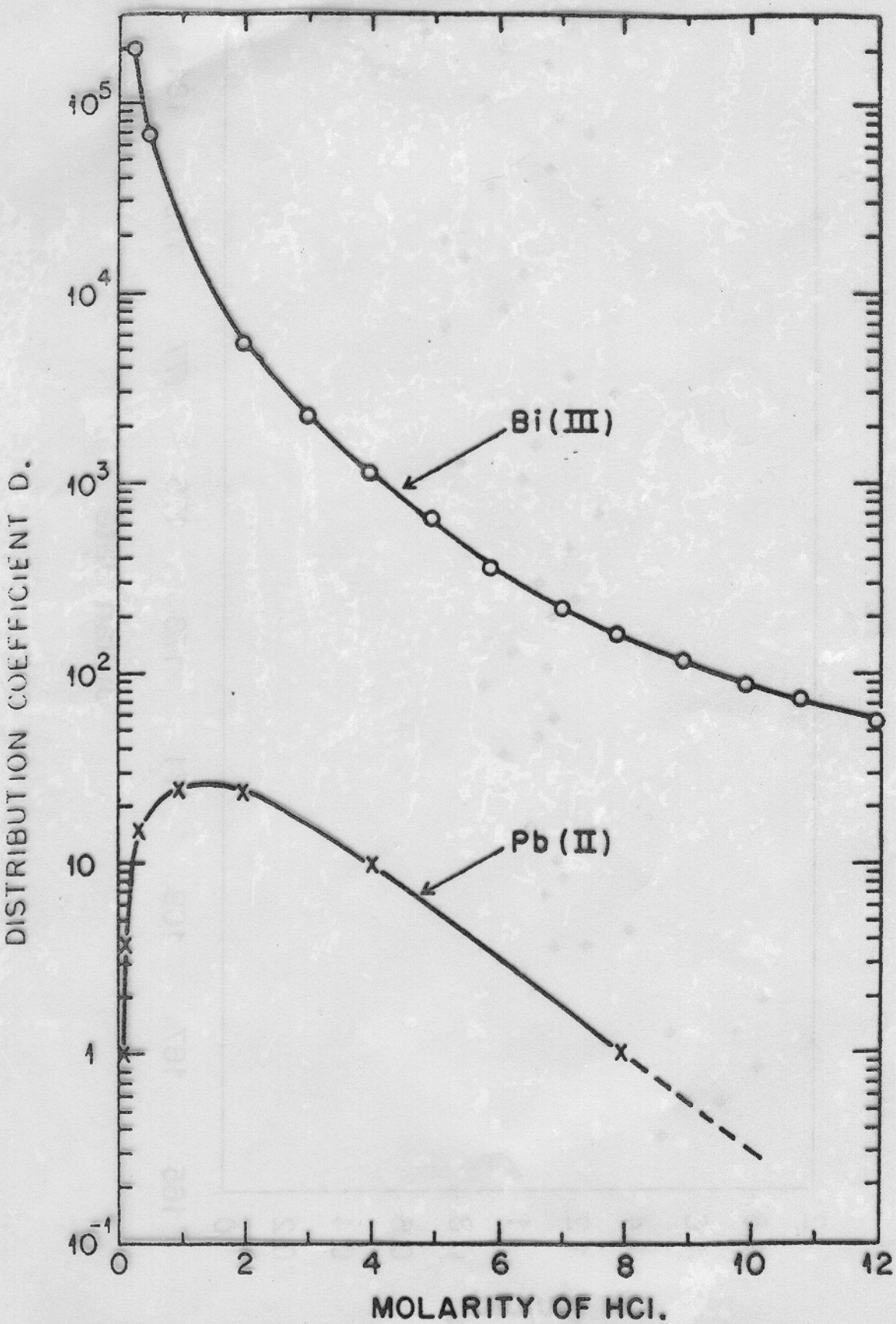
(adapted from Nevissi, A.E. 1991, J. Radioanal. Nucl. Chem.)

NEED TO SIMPLIFY METHOD

Existing Methods are too complex
See two following examples

Chloride Complexes!

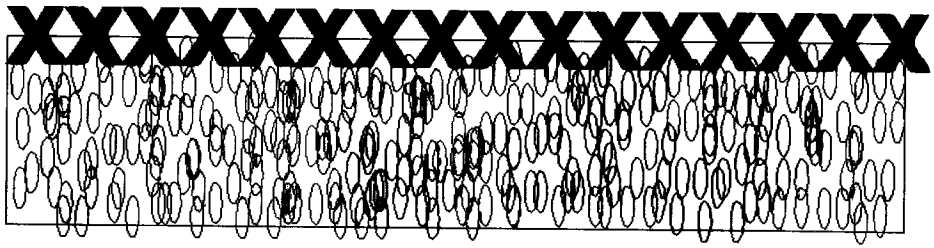
Adsorption of Pb(II) and Bi(III) onto anion resin from HCl Solution



F. Nelson and K.A. Kraus, J. Am. Chem. Soc. (1954) 76, 5916-5920.

ADVANTAGES OF MEMBRANE FILTERS

Small anion exchange beads- high surface area
Size - Amenable for Direct Counting
Reasonably high flow rates



Mostly Surface Deposited

Beta Counting Efficiency - Bi-210 - 40%
Alpha Counting Efficiency - Po-210 - 17%

Separation of Pb from Bi and Po by Anion Membrane Filtration

1. Filter in 50% HNO_3, gentle heat for 24 hrs.
2. Remove Filter – water wash, Dry.
3. Add 20 ml 1.0 M HCl. Warm to dissolve.
4. Cool. Prefilter with 0.45 micron glass filter (if necessary).
5. Filter slowly (1-3 ml/min) through anion membrane.
6. Rinse well with 1 M HCl to remove Pb.
7. Dry at 60 C.
8. Neutralize H^+ with vapors from 50 % NH_4OH for 5 min.
9. Place membrane in beta/alpha counter ($^{210}Bi/^{210}Po$)

^{210}Pb in sample (in wash) left for approx. 1-2 months to reequilibrate ^{210}Bi for ^{210}Pb determination.

PROBLEMS

WIND BLOWN DUST – SOIL COMPONENT

COAL FIRED POWER PLANTS – FLY ASH?

WOOD SMOKE ?

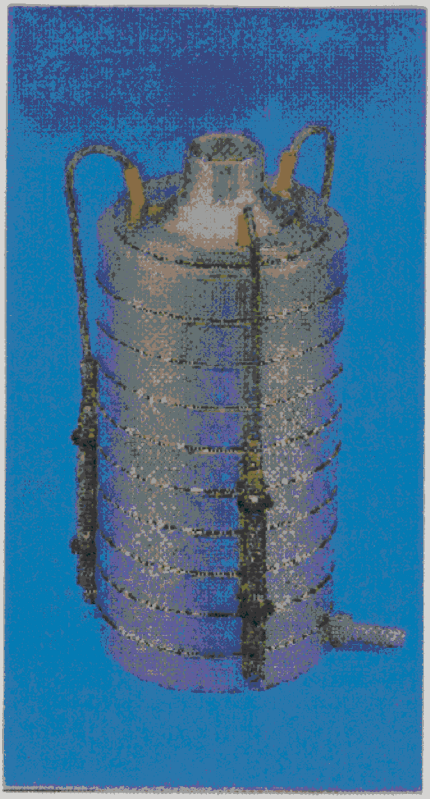
TOTAL SUSPENDED PARTICULATE SAMPLES

POSSIBLE ANSWER: SIZE FRACTIONATED SAMPLES

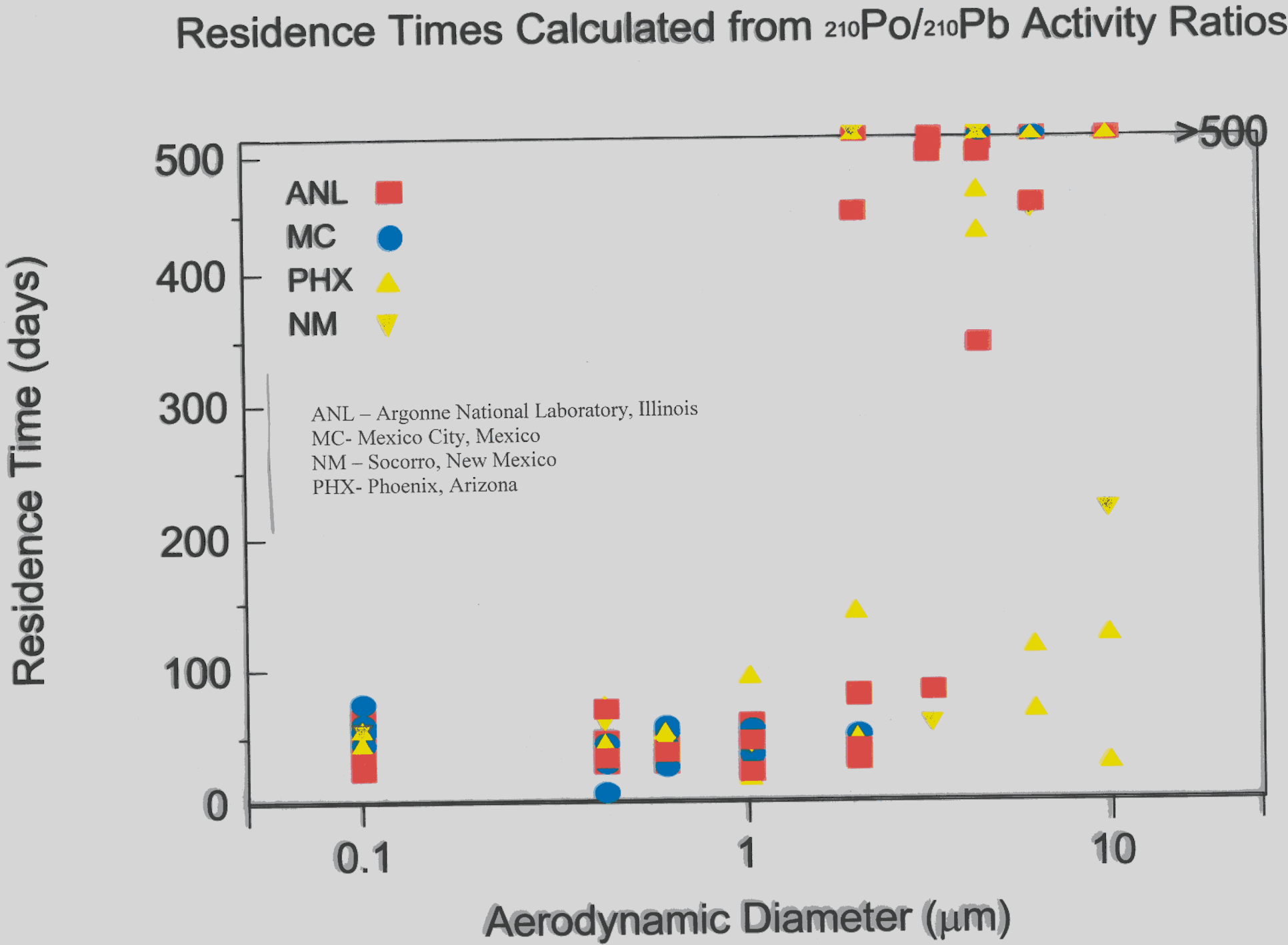
NEED SUITABLE METHOD!

Graseby-Anderson Model 20-800 Impactor
Operated at a flow rate of 0.028 m^3/min (1 scf/min)

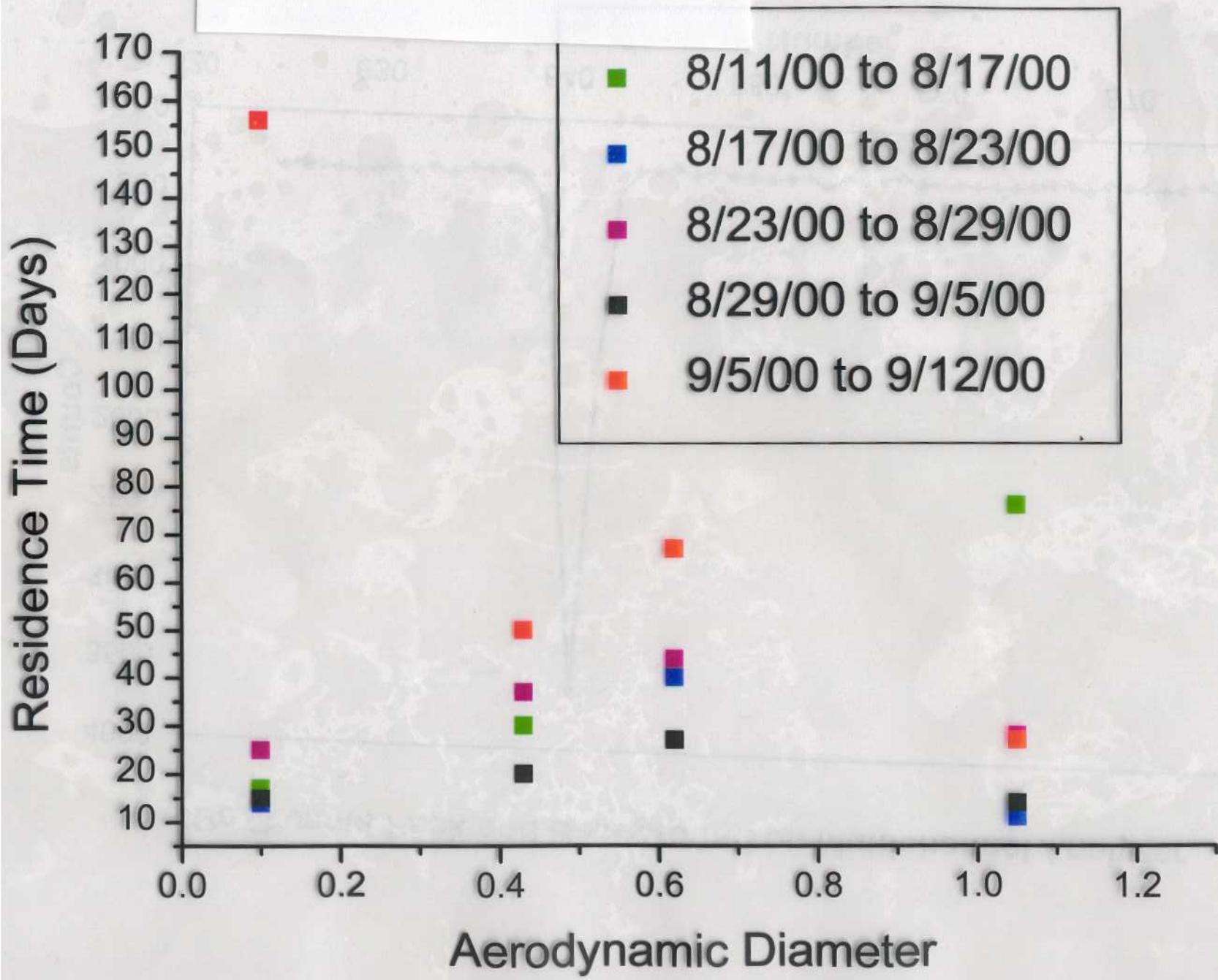
Teflon Sheet Collection – 8 stages
Quartz final filter



The cut off diameter for each stage of the impactor used in this study was 9.2 μm, 5.8 μm, 4.2 μm, 3.1 μm, 2.0 μm, 1.05 μm, 0.62 μm, 0.43 μm, and 0.1 μm


Residence Times Calculated from 210Po/210Pb Activity Ratios
Residence Time (days)
500
400
300
200
100
0
>500
ANL
MC
PHX
NM
ANL – Argonne National Laboratory, Illinois
MC- Mexico City, Mexico
NM – Socorro, New Mexico
PHX- Phoenix, Arizona
0.1
1
10
Aerodynamic Diameter (μm)

Deer Park, Texas (Texas 2000 Air Quality Study)



Aerosol residence times calculated from the $^{210}Po/^{210}Pb$ ratios for samples collected at Centerton, NJ.

Date	D (μm)	$^{210}Po/^{210}Pb$	Age (days)
7/24-7/30	9.2	0.112	32
	5.8	0.139	39
	4.2	0.142	40
	3.1	0.107	31
	2.0	0.177	50
	1.05	0.156	44
	0.62	0.125	35
	0.43	0.101	29
	0.1	0.132	37
7/30-8/ 6	9.2	0.131	37
	5.8	0.095	27
	4.2	0.144	41
	3.1	0.159	45
	2.0	0.106	30
	1.05	0.156	44
	0.62	0.094	27
	0.43	0.085	25
	0.1	0.069	20
8/6-8/12	9.2	-	-
	5.8	0.156	44
	4.2	0.137	39
	3.1	0.125	35
	2.0	0.129	36
	1.05	0.133	37
	0.62	0.110	31
	0.43	0.136	39
	0.1	0.138	39

Sierra Impactor – Stage 4 used for 1 micron cutoff – 24 hr. samples

Apparent Ages for Aerosols – NETL

Sample	SIZE(μm)	CORR. AGE (days)
PA1	<1	17
PA2	>1	11
PA5	<1	19
PA6	>1	20
PA9	<1	21
PA10	>1	12
PA11	<1	18
PA12	>1	15
PA13	<1	30
PA14	>1	27
PA17	<1	10
PA18	>1	30
PA21	<1	12
PA22	>1	25
PA25	<1	24
PA26	>1	32
PA29	<1	31
PA30	>1	46

Apparent Ages for Aerosols – Schenley Park (SP)

Sample	SIZE(μm)	CORR. AGE (days)
PA3	<1	13
PA4	>1	23
PA7	<1	14
PA8	>1	22
PA15	<1	24
PA16	>1	36
PA19	<1	37
PA20	>1	32
PA23	<1	15
PA24	>1	28
PA27	<1	20
PA28	>1	25

Comparison of AGES

Centerton, NJ – Summer 1999
Rural Site

< 1 micron

33 ± 6 days

Pittsburgh (SP and NETL) – Summer 2001

Suburban

23 ± 7 days

NO EVIDENCE OF EXCESS ^{210}Po!!!!!

Some Comments:

Apparent Ages – Distribution of Ages!

Example – 90 % 10 day lifetime = 9 days
10 % 100 day lifetime = 10 days

Apparent Lifetime = 19 days

Or..... 20 % 50 day lifetime = 10 days
80 % 10 day = 8 days
= 18 days

CHEMICAL COMPOSITION!

SULFATES AND NITRATES ARE WATER SOLUBLE

Will wash out – Precipitation Measurements on Rain and Hail Indicate 10 Day Residence times.

What is giving us the longer residence times?

Likely Answer:

Carbonaceous Soots – Especially Oily Soot Particles

Carbonaceous Aerosols

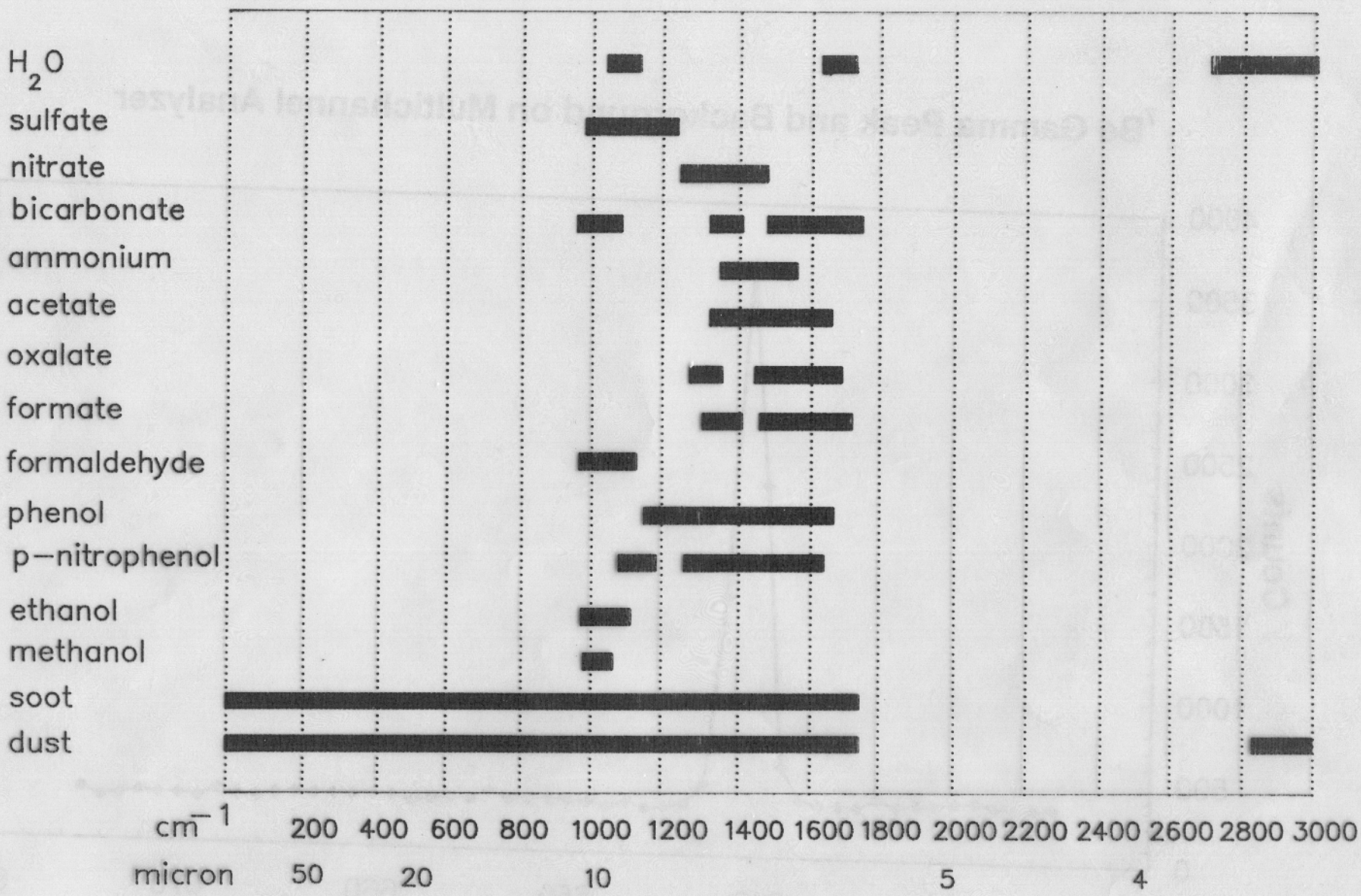
Important Radiative Absorbers

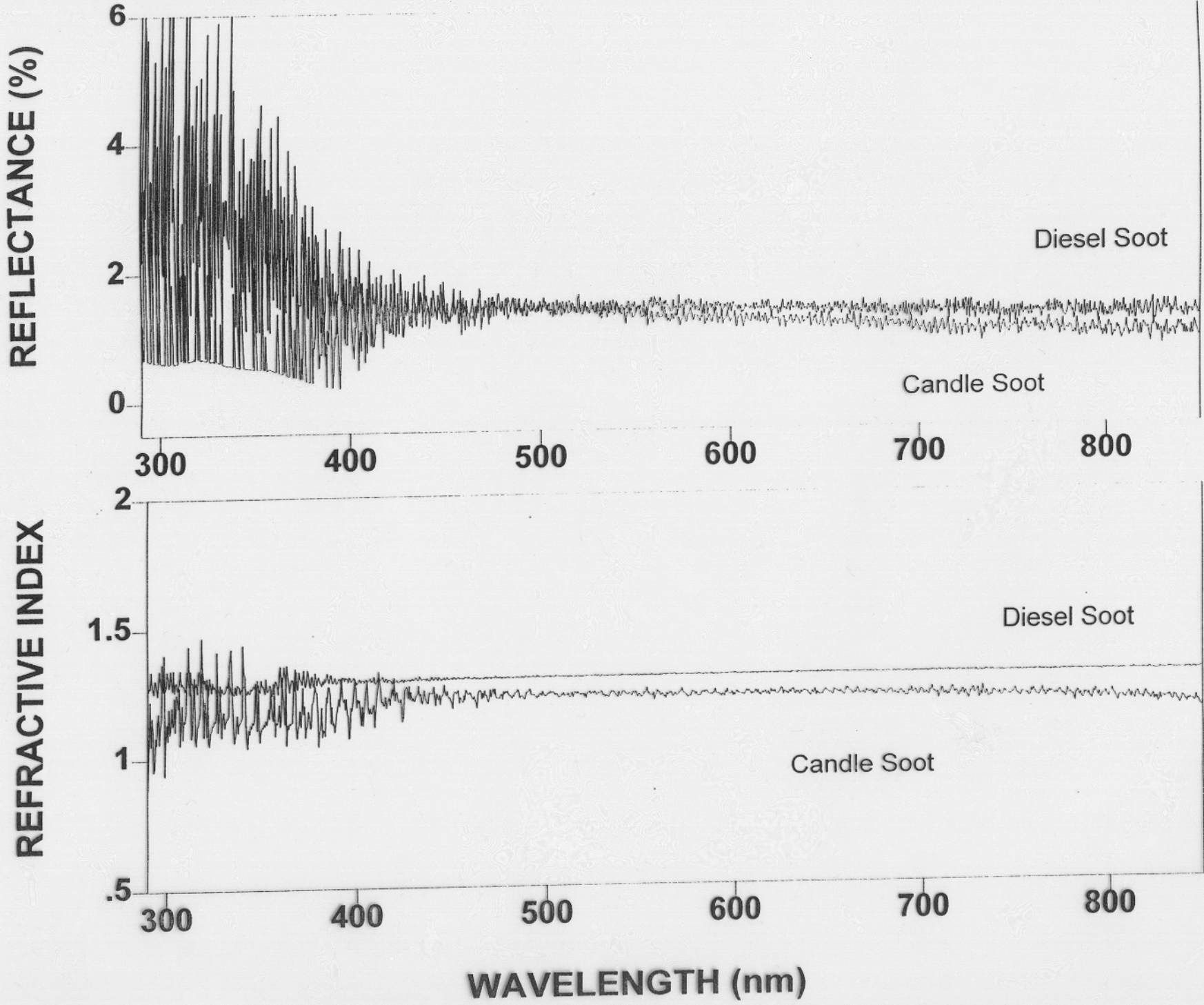
Long-wave and Short-wave Radiation

Have Climate – Urban and Regional Impacts – as well as Health Impacts

Urban Heat Island stresses may amplify health impacts of aerosol and other pollutants!

SPECTRAL LOCATIONS OF THE MAJOR INFRARED ABSORPTION BANDSFOR THE AEROSOL SPECIES




REFLECTANCE (%)
6
4
2
0
Diesel Soot
Candle Soot
300
400
500
600
700
800
REFRACTIVE INDEX
2
1.5
1
.5
Diesel Soot
Candle Soot
300
400
500
600
700
800
WAVELENGTH (nm)

Conclusions

Natural Radioactivity can be useful for tracing aerosols and estimation of lifetimes.

Carbonaceous soots may be playing important role. They are produced from combustion, especially diesel engines.

Aerosols need to be better chemically and physically characterized. Radioactivity can be useful in helping to determine sources. Example: 210Po/210Pb as indicator of soil contribution in larger aerosol size range! (Note: little indication of major soil component in Pittsburgh samples, while good indication important in Phoenix and in Mexico City).

Center for Environmental Science- New Initiative – Focus on Aerosol/Urban Climate/Asthma connections – Univ. of Chicago/Argonne National Laboratory!

Carbonaceous Aerosols important absorbers – Climate implications.

24 hr. Pittsburgh data indicate no major sources of 210Po in the larger size ranges – i.e. low impact of soils.

Low 210Po/210Pb also in larger size ranges indicates little “fly-ash” Po source previously suggested.

Method looks to be a good means of soil derived aerosol components in >1 micron aerosol and residence times for <1 micron aerosol!

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